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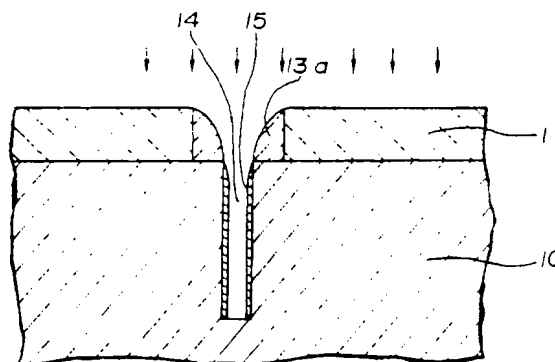
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(54) **Dry etching methods.**

(57) A dry etching process utilizes a gas for forming a side wall protective layer (15) when etching a trench (14) in monocrystalline silicon, the gas comprising a base etching gas to which is added at least chlorine trifluoride, or in the alternative silicon and fluorine.

**FIG.2 (B)**



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## DRY ETCHING METHODS

This invention relates to dry etching methods applicable to anisotropic etching in semiconductor manufacture, and to composite gases for such methods.

Silicon trench etching is important in ultra-large LSI (ULSI) manufacture of high mega-bit DRAMs and high speed bipolar devices. For performing the etching process, various etching gases have been developed and used. Typically, fluorine (F) type gas, chlorine (Cl) type gas, or a mixture thereof are used. For example, Japanese patent (unexamined) publication (Tokkai) 63/73526 discloses an etching method utilizing  $\text{SiCl}_4/\text{N}_2$  type gas.

In a dry etching method for monocrystalline silicon, an  $\text{SiO}_2$  mask is formed on the inner periphery perpendicular to the plane of a monocrystal substrate, and then etching is performed with  $\text{SiCl}_4/\text{N}_2$  type etching gas. In this process,  $\text{Si}_3\text{N}_4$  formed as a reaction product during the etching process is used as a protective layer when forming a trench.

However, there are problems with such methods.

Firstly, the reaction product forming the protective layer, can obstruct etching and lower the etching speed or efficiency. Secondly, in a batch type etcher, the etching rate or efficiency can be lowered due to a loading effect. To solve such problems of low efficiency, it has been proposed in "1988 Shuuki Obutsu" 7a-K-7 to use  $\text{SF}_6/\text{SiCl}_4/\text{N}_2$  type etching gas, but this can cause contamination.

On the other hand, when the required pattern cannot be formed by a lithographic process and has to be patterned by a self-alignment process, the self-alignment process is performed by forming side walls of  $\text{SiO}_2$  with tetraethoxysilane, and then etching using the side walls as a mask. However, tapers on the side walls may cause scattering of an injected ion beam, so causing scoop or under-cut immediately beneath the mask.

According to the present invention there is provided a composite gas for dry etching to form a desired configuration of trench in monocrystalline silicon, the gas being composed of:

a base composite gas for etching the monocrystalline silicon; and an additive gas added to said base composite gas and containing at least  $\text{ClF}_3$  for forming a protective layer on the side wall of said trench.

According to the present invention there is also provided a composite gas for dry etching to forming a desired configuration of trench in monocrystalline silicon, the gas being composed of:

a base composite gas for etching the monocrystalline silicon; and an additive gas added to said base

composite gas, and containing at least Si and F as components.

According to the present invention there is also provided a dry etching process for forming a trench in monocrystalline silicon, the process comprising the steps of:

forming an opening in an  $\text{SiO}_2$  layer formed on a monocrystalline silicon substrate;

performing etching utilizing the residual  $\text{SiO}_2$  layer as a masking layer and with an etching gas, which is composed of:

a base composite gas for etching the monocrystalline silicon; and an additive gas added to said base composite gas, said additive gas containing at least  $\text{ClF}_3$  for forming a protective layer on the side wall of said trench.

According to the present invention there is also provided a dry etching process for forming a trench in monocrystalline silicon, the process comprising the steps of:

forming an opening in an  $\text{SiO}_2$  layer formed on a monocrystalline silicon substrate;

performing etching utilizing the residual  $\text{SiO}_2$  layer as a masking layer and with an etching gas, which is composed of:

a base composite gas for etching the monocrystalline silicon; and an additive gas added to said base composite gas, said additive gas being containing at least Si and F as components.

The invention will now be described by way of example with reference to the accompanying drawings, throughout which like parts are referred to by like references, and in which:

Figures 1(A), 1(B) and 1(C) are sections showing stages in a dry etching process according to the invention; and

Figures 2(A) and 2(B) are sections showing stages in another dry etching process according to the invention.

Referring to Figures 1(A), 1(B) and 1(C), a preferred etching process will be discussed in terms of etching a monocrystalline silicon substrate. An  $\text{SiO}_2$  layer 11 is formed on a monocrystalline silicon substrate 10. On the  $\text{SiO}_2$  layer 11, a resist layer 12 is formed and defines an opening where a trench 14 is to be formed, as shown in Figure 1(A). The opening in the resist layer 12 is formed by a known patterning process.

Then, utilizing the resist layer 12 as a mask, reactive ion beam etching (RIE) is used to form an opening 11a through the  $\text{SiO}_2$  layer 11, as shown in Figure 1(B). After forming the opening 11a, the resist layer 12 is removed. Then, the trench 14 of a desired depth is formed by a bias charge type ECR etching device, as shown in Figure 1(C). Dur-

ing this etching process, the SiO<sub>2</sub> layer 11 serves as a mask.

The etching process for forming the trench 14 is performed in the following conditions. The pressure is set at 10 mTorr (0.013 Pascal). RF bias is applied at 300W. SiCl<sub>4</sub>/N<sub>2</sub> type gas is used for forming a side wall protective layer 15. In order to improve the etching rate, 10% of ClF<sub>3</sub> is added.

It has been found that radical fluorine (F<sup>\*</sup>) and radical chlorine (Cl<sup>\*</sup>) generated by dissociation of ClF<sub>3</sub> serve to improve the etching rate. Therefore, the presence of ClF<sub>3</sub> in the gas for forming the protective layer 15 may compensate lowering of the etching rate due to loading effect. As a result, even when the area on which etching is performed is so wide as possibly to cause loading effect, the etching rate can be maintained at satisfactorily high level.

It will be appreciated that the bonding energy of ClF<sub>3</sub> is Cl-F = 61.4 Kcal/mol, which is smaller than SF<sub>6</sub> (SF = 90 Kcal/mol), NF<sub>3</sub> (N-F = 63 Kcal/mol) and CF<sub>4</sub> (C-F = 107 Kcal/mol). As can be seen herefrom, since ClF<sub>3</sub> has a smaller bonding energy than other gases, Cl<sup>\*</sup> and F<sup>\*</sup> can be obtained more easily therefrom.

It should be appreciated that although the gas used in the preferred process is specified to be SiCl<sub>4</sub>/N<sub>2</sub> type gas to which ClF<sub>3</sub> is added, any appropriate gas, such as Cl<sub>2</sub>/N<sub>2</sub> type, Cl<sub>2</sub>/O<sub>2</sub> type, Br<sub>2</sub>/N<sub>2</sub> type, HBr/N<sub>2</sub> type or SiCl<sub>4</sub>/O<sub>2</sub> type gases, can be used as replacements for the specific gas. Therefore, the type of the gas to which ClF<sub>3</sub> is added, is to be considered not essential to the subject matter of the invention. Furthermore, although the content of ClF<sub>3</sub> is specified as 10%, the content is variable in a range of 1% to 90%. In addition, as the gas for performing etching while forming a protective layer on the side wall, a gas composed of chlorine, bromine and compounds thereof can also be used. As above, can be added to the gas in the ClF<sub>3</sub> content of 1% to 90%. Furthermore, it is possible to add a rare gas.

Figures 2(A) and 2(B) show another preferred process for implementing the present invention. In Figure 2(A), the silicon substrate 11 is formed with an SiO<sub>2</sub> layer 11 of thickness 1.0μm. An opening 11a having a greater diameter than the desired diameter of a trench 14 is formed through the SiO<sub>2</sub> layer 11. In this example, the diameter of the opening 11a is 1.0μm. For this substrate, chemical vapour deposition (CVD) is performed utilizing TEOS gas as the source gas for forming an SiO<sub>2</sub> layer 13 of thickness 400 nm. Then, etch-back treatment is performed for forming a side wall 13a on the side wall of the opening 11a. The internal diameter of the side wall 13a is 0.3μm. The side wall 13a has 60° to 70° of taper due to the influence of the etch-back.

Thereafter, utilizing the TEOS layer and the SiO<sub>2</sub> layer 11 as a mask, etching is performed by mean of bias charge type ECR etching apparatus for forming a desired depth of the trench 14, as shown in Figure 2(B). In this etching process, a side wall protective layer 15 is formed.

The following are the conditions for performing etching for forming the trench. As an etching gas, a mixture gas of SiCl<sub>4</sub>, N<sub>2</sub> and SiF<sub>4</sub> is used. These gases are supplied at a flow rate ratio of SiCl<sub>4</sub>/N<sub>2</sub>/SiF<sub>4</sub> = 10 SCCM/10 SCCM/10 SCCM. The pressure is set at 10 mTorr (0.013 Pascal), the microwave power is set as 850W, and Vdc is set at -250V. During this etching process, F<sup>\*</sup> is generated from the SiF<sub>4</sub> to prevent lowering of the etching rate. Furthermore, the Si in the SiF<sub>4</sub> may serve to protect the side wall, so avoiding scoop and undercut. Therefore, with this process, the desired configuration of the trench can be formed.

The specific gas SiF<sub>4</sub>, that is an Si and F containing gas, can be added not only for the specified combined gas but also for other combinations of gases, such as Br<sub>2</sub>/N<sub>2</sub>. In the later case, the SiF<sub>4</sub> is added in the flow rate ratio of Br<sub>2</sub>/N<sub>2</sub>/SiF<sub>4</sub> = 10 SCCM/10 SCCM/10 SCCM. When etching is performed with the conditions set forth above, an equivalent result can be obtained.

## Claims

1. A composite gas for dry etching to form a desired configuration of trench (14) in monocrystalline silicon, the gas being composed of:  
a base composite gas for etching the monocrystalline silicon; and an additive gas added to said base composite gas and containing at least ClF<sub>3</sub> for forming a protective layer (15) on the side wall of said trench (14).
2. A composite gas according to claim 1 wherein said base composite gas is SiCl<sub>4</sub>/N<sub>2</sub> type gas, Cl<sub>2</sub>/N<sub>2</sub> type gas, Cl<sub>2</sub>/O<sub>2</sub> type gas, Br<sub>2</sub>/N<sub>2</sub> type gas, HBr/N<sub>2</sub> type gas or SiCl<sub>4</sub>/O<sub>2</sub> type gas.
3. A composite gas according to claim 1 or claim 2 wherein said additive gas is added to the base composite gas in a range of 1 to 90%.
4. A composite gas for dry etching to forming a desired configuration of trench (14) in monocrystalline silicon, the gas being composed of:  
a base composite gas for etching the monocrystalline silicon; and an additive gas added to said base composite gas, and containing at least Si and F as components.
5. A composite gas according to claim in wherein said base composite gas is SiCl<sub>4</sub>/N<sub>2</sub> type gas or Br<sub>2</sub>/N<sub>2</sub> type gas.
6. A composite gas according to claim in or claim 5 wherein said additive gas is SiF<sub>4</sub> gas.

7. A dry etching process for forming a trench (14) in monocrystalline silicon, the process comprising the steps of:

forming an opening (11a) in an SiO<sub>2</sub> layer (11) formed on a monocrystalline silicon substrate (10);  
performing etching utilizing the residual SiO<sub>2</sub> layer (11) as a masking layer and with an etching gas, which is composed of:

a base composite gas for etching the monocrystalline silicon; and an additive gas added to said base composite gas, said additive gas containing at least ClF<sub>3</sub> for forming a protective layer (15) on the side wall of said trench (14).

8. A process according to claim 7 wherein said base composite gas is SiCl<sub>4</sub>/N<sub>2</sub> type gas, Cl<sub>2</sub>/N<sub>2</sub> type gas, Cl<sub>2</sub>/O<sub>2</sub> type gas, Br<sub>2</sub>/N<sub>2</sub> type gas, HBr/N<sub>2</sub> type gas or SiCl<sub>4</sub>/O<sub>2</sub> type gas.

9. A process according to claim 7 wherein said additive gas is added to the base composite gas in a range of 1 to 90%.

10. A dry etching process for forming a trench (14) in monocrystalline silicon, the process comprising the steps of:

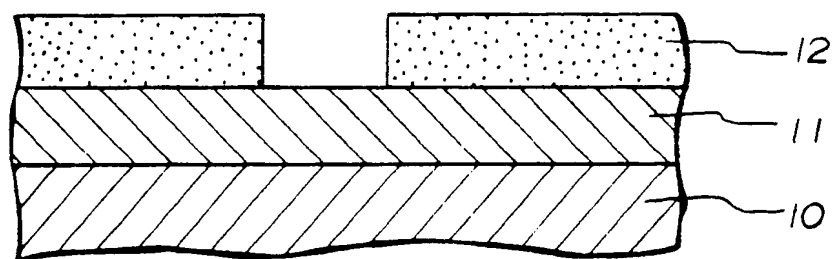
forming an opening (11a) in an SiO<sub>2</sub> layer (11) formed on a monocrystalline silicon substrate (10);  
performing etching utilizing the residual SiO<sub>2</sub> layer (11) as a masking layer and with an etching gas, which is composed of:

a base composite gas for etching the monocrystalline silicon; and an additive gas added to said base composite gas, said additive gas being containing at least Si and F as components.

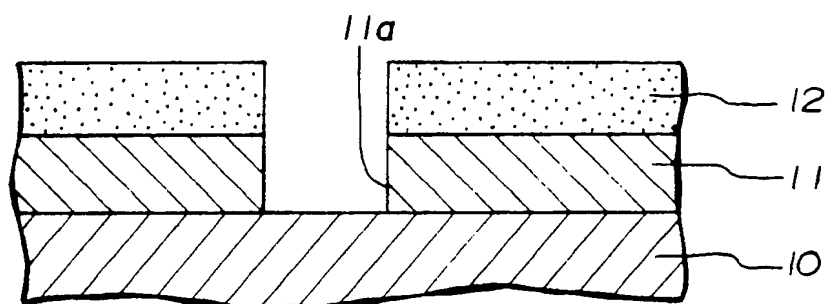
11. A process according to claim 10 wherein said base composite gas is SiCl<sub>4</sub>/N<sub>2</sub> type gas or Br<sub>2</sub>/N<sub>2</sub> type gas.

12. A process according to claim 10 wherein said additive gas is SiF<sub>4</sub> gas.

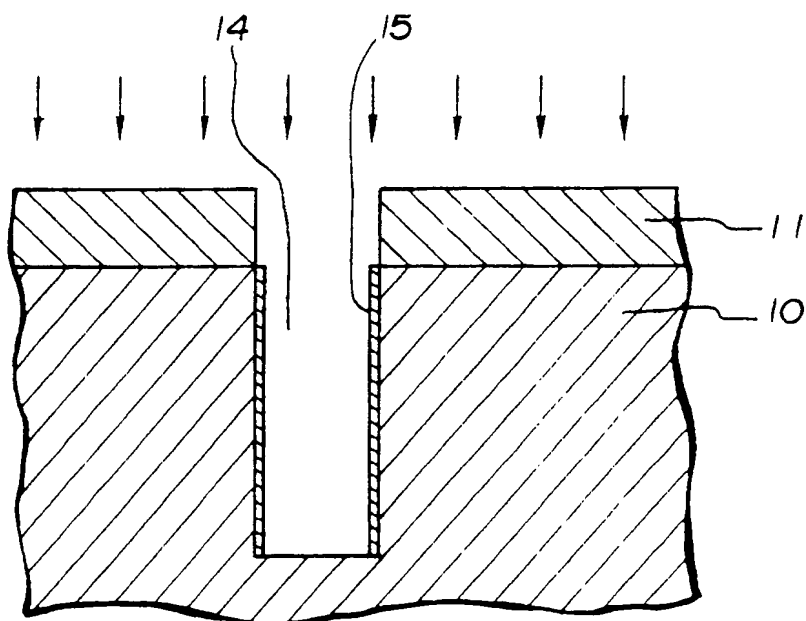
**FIG. 1 (A)**



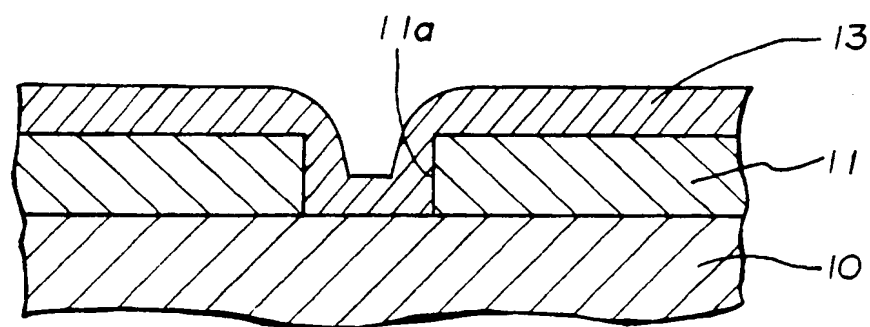
**FIG. 1 (B)**



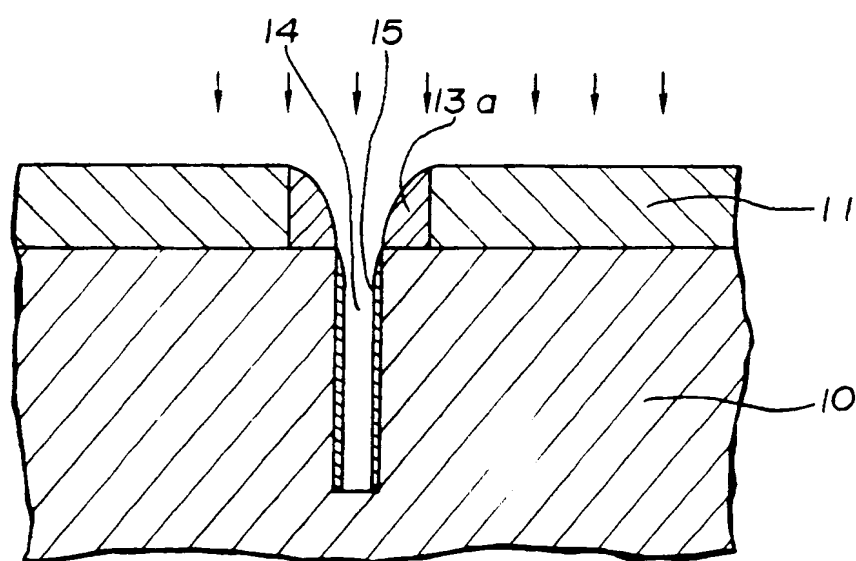
**FIG. 1 (C)**



**FIG. 2 (A)**



**FIG. 2 (B)**





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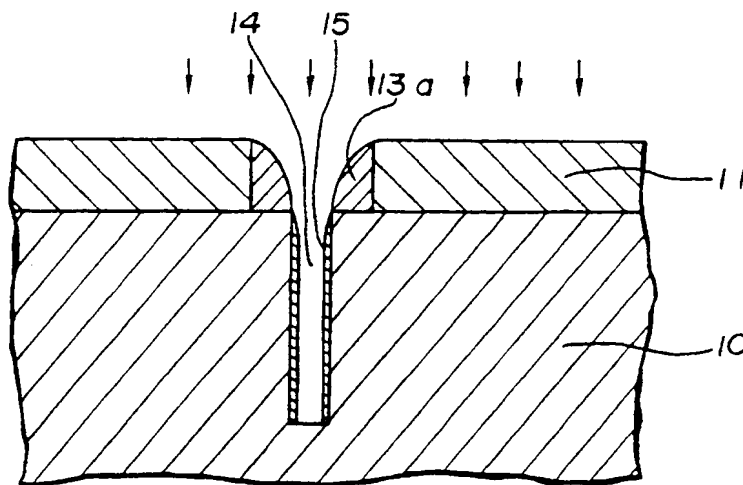
(71) Applicant: SONY CORPORATION

(54) Dry etching methods.

(57) A dry etching process utilizes a gas for forming a side wall protective layer (15) when etching a trench (14) in monocrystalline silicon, the gas comprising a base etching gas to which is added at least

chlorine trifluoride, or in the alternative silicon and fluorine.

### FIG.2 (B)



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# EUROPEAN SEARCH REPORT

Application Number

EP 90 30 7877

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claims	CLASSIFICATION OF THE APPLICATION (Int. Cl. 5)
Y	US-A-4 784 720 (TEXAS INSTRUMENTS) * Column 7, line 60 - column 9, line 57; claims *	1-3,7-9	H 01 L 21/306 H 01 L 21/308
A	---	2,8	
Y	WO-A-8 102 947 (WESTERN ELECTRIC) * Page 10, line 32 - page 11, line 34 *	1-3,7-9	
X	WO-A-8 502 818 (ADVANCED MICRO DEVICES) * Claims *	4,6,10,12	
A	* Page 8, line 1 - page 10, line 14 *	1-3,7-9	
A	US-A-4 690 729 (TEXAS INSTRUMENTS) * Column 6, line 41 - column 7, line 54 *	2,8	
P,A	US-A-4 885 054 (ANELVA CORP.) * Column 5, lines 33-37; claims *	1-3,7-9	
X	EP-A-0 272 143 (APPLIED MATERIALS) * Page 6, lines 25-41; tables *	4,6,10,12	TECHNICAL FIELDS SEARCHED (Int. Cl. 5)
A	* Page 9, line 38 - page 10, line 45 *	5,11	H 01 L
A	EP-A-0 036 144 (IBM) * Abstract *	4-6,10-12	
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The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 05-02-1991	Examiner GORI P.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	

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### CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing more than ten claims.

- ☐ All claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for all claims.
- ☐ Only part of the claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims and for those claims for which claims fees have been paid, namely claims:
- ☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims.

### X LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirement of unity of invention and relates to several inventions or groups of inventions, namely:

See sheet -B-

- ☒ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.
- ☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:
- ☐ None of the further search fees has been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:



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EP 90 30 7877 -B-

#### LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirement of unity of invention and relates to several inventions or groups of inventions,

namely:

1. Claims 1-3,7-9: A gas, producing sidewall protection deposits in the etching of silicon, and containing an additive ( $\text{ClF}_3$ ); a process for etching trenches using said gas.
2. Claims 4-6,10-12: A gas for etching silicon, containing an additive based on  $\text{Si}^*\text{F}$ ; a process for etching trenches using said gas.